A REVIEW OF THE CONTRASTING BEHAVIOR OF TWO MAGMATIC VOLATILES: CHLORINE AND CARBON DIOXIDE

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Abstract

Chlorine (Cl) and carbon dioxide (CO_2) are common magmatic volatiles with contrasting behaviours. CO_2 solubility increases with pressure whereas Cl solubility shows relatively little pressure or temperature effect. CO_2 speciation changes with silicate melt composition, dissolving as carbonate in basaltic magmas and molecular CO_2 in more silicic compositions. In H_2O-bearing systems, the strongly non-ideal behavior of alkali chlorides causes unmixing of the volatile phase to form a H_2O-rich vapor and a hydrosaline phase with important implications for the maximum concentration of Cl in magmas. Addition of CO_2 to the magma hastens immiscibility at crustal pressures (< 500 MPa), inducing the formation of CO_2-rich vapors and Cl-rich hydrosaline melts.

Keywords: Chlorine, Cl, carbon dioxide, CO_2, volatiles, magma

1. Introduction

Besides H_2O, CO_2 and Cl are two of the most abundant magmatic volatiles and are notably present in fluid inclusions associated with magmatic-hydrothermal ore deposits. They also provide an interesting contrast in their behavior during magmatic fractionation and degassing. Whereas CO_2 increases linearly in concentration until reaching saturation as a gas phase, Cl behaves in an extremely non-ideal manner and partitions into the exsolving fluids primarily as a salt complex. The coexistence of CO_2 and Cl in volatile-saturated magmatic systems will often induce unmixing to form multiple phases (e.g., vapors and hydrosaline melts). This review explores some of the chemical characteristics of these two magmatic volatiles.

2. The Speciation of CO_2 in silicate melts

Workers have long known that CO_2 was about an order of magnitude less soluble than H_2O in silicate melts, although it was not until the 1970's that studies began on the mechanism of CO_2 incorporation within magmas. Mysen et al. (1975) used ^{14}C beta-track mapping techniques to study the solubility of CO_2 gas in a variety of natural melt compositions and found that it dissolves both as carbonate and molecular CO_2. Researchers later confirmed that CO_2 dissolves solely as carbonate in basaltic melts including mafic alkaline magmas such as basanites, leucitites and nephelinites (Blank & Brooker, 1994). In contrast, only molecular CO_2 is found in rhyolites (Fogel & Rutherford, 1990). Intermediate compositions (e.g., andesites) have both species present (Mysen et al., 1975; King et al., 1996) as is the case for evolved silica-undersaturated magmas such as phonolites (Blank & Brooker, 1994).

CO_2 dissolves as carbonate in mafic melts, its solubility dependent on the nature and abundance of complexing cations such as Ca, K and Na (Dixon, 1997). As a result, carbonate is far more soluble in alkaline basalts than in tholeiites. In contrast, CO_2 does not react with the melt as it dissolves in molecular form, so there should be little variation in CO_2 solubility in felsic magmas.

Moreover, on a molar basis, CO_2 solubility changes little with melt composition along the tholeiitic basalt-rhyolite join (Blank & Brooker, 1994; see also Fig. 1 below).
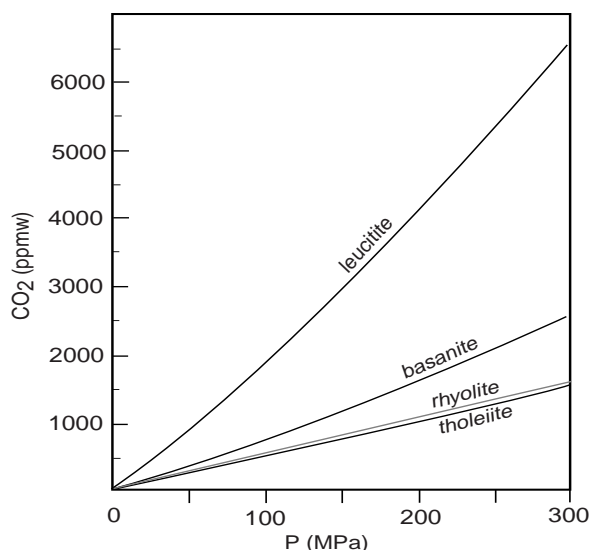

Fig.1. Solubility of total CO_2 (molecular + carbonate) as a function of pressure for four magma compositions. Leucitite, basanite and tholeiitic basalt calculated from parameters of Holloway & Blank (1994) at 1200°C. Rhyolite curve from data of Fogel & Rutherford (1990) at 1150°C.

3. Temperature, pressure and CO_2 solubility

In all magmas, CO_2 solubility increases linearly with pressure (Fig. 1). Temperature effects depend on the mechanism of incorporation of CO_2 into the melt (Stolper et al., 1987). In rhyolitic magmas, CO_2 solubility decreases as temperature increases (see Fig. 4 in Fogel & Rutherford, 1990). This is consistent with the typical inverse correlation between molecular gas solubility and temperature. Exceptions occur when gases dissolve by interacting with melt to form charged complexes such as carbonate which exhibit a positive correlation of solubility with temperature. The temperature effect on solubility is very small compared with the effects of melt composition and pressure (Blank & Brooker, 1994).

The solubility of CO_2 also depends on the composition of the volatile phase. Blank et al. (1993) showed that Henry's Law applies for the

H_2O-CO_2-rhyolite system at pressures <100 MPa. In a melt-vapor system where the vapor contains two components (i.e., CO_2 and H_2O), addition of one gas dilutes the other, decreasing its activity and thereby its concentration (solubility) in the

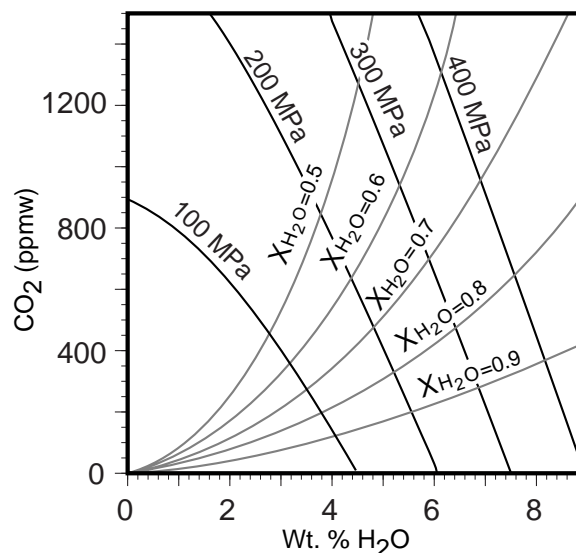Fig. 2. Solubility plot for system rhyolite-H_2O-CO_2 at 675°C. Lines labeled with units of pressure represent isobars that display solubility of H_2O and CO_2 as function of fluid composition. Isopleths labeled with units of X_{H2O} display the composition of vapor in equilibrium with the melt. See Holloway & Blank (1994) for a discussion of similar diagrams.

melt. In other words, addition of H_2O to a melt-CO_2 system decreases the solubility of CO_2. This is illustrated in Fig. 2 where the solubility of CO_2 at fixed temperature and pressure varies with vapor composition in the H_2O-CO_2-melt system. There is some controversy whether this Henrian behavior continues at high pressures (>500 MPa; e.g., Mysen et al., 1975) due to the possible depolymerizing effect of H_2O on melt structure (cf. Stolper et al., 1987).

4. The solubility of Cl in silicate melts

Chlorine "saturation" is an ambiguous term, literally implying saturation with Cl_2 gas or Cl^- ion. Similarly, when most workers discuss sulfur saturation, they intend to refer not to native S, but to saturation with either a sulfide phase (pyrrhotite) or a sulfate phase (anhydrite). With

respect to Cl, there is no phenocryst phase with a high and fixed Cl concentration that represents a "saturating" phase. As a result, Cl concentrations will increase with fractionation unless a phase exsolves into which Cl can partition.

Experimental studies of Cl solubility (e.g., Webster, 1997) are conducted by adding alkali chlorides to the melt. If the system is anhydrous or H_2O-poor, the melt becomes saturated with a salt melt, consisting of Cl complexed to Na, K, Fe, etc. In H_2O-bearing systems, to a first approximation, the concentration of Cl in exsolved H_2O vapor increases sympathetically with that of Cl in the silicate phase. However, as the concentration of Cl becomes higher, the system becomes strongly non-Henrian and Cl content in the volatile phase increases more rapidly than that in the melt (Carroll & Webster, 1994). The non-ideality of the system becomes marked in the pressure-temperature region near that for subcritical behavior in the system NaCl-H_2O. Within that region, the Cl concentration in the melt becomes fixed. This is because at magmatic temperatures and shallow crustal pressures (e.g., at 800°C and pressures $\leq$ 140 MPa), the binary system NaCl-H_2O is characterized by a miscibility gap whereby the fluid unmixes to form a low-density vapor and a high-density hydrosaline melt (brine). Addition of silicate melt to the system cannot undo this reality of phase behavior. Because the compositions of the vapor and hydrosaline phase are invariant for a given temperature and pressure (Sourirajan & Kennedy, 1962), so too must be the Cl concentration of the silicate melt (Fig. 3). Further addition of Cl to the system results in changes in the relative proportions of the phases, but not in their compositions (i.e., more of the hydrosaline phase is produced). Traditional partition coefficients (XCl in vapor/XCl in melt) thus become meaningless (Candela & Piccoli, 1995).

In essence, this "buffering" of Cl concentration in the silicate melt is the same as if a Cl-bearing crystal of fixed composition were present in the system (such as anhydrite for S-bearing magmas). The actual concentration of Cl in the "buffered" magma will be a function of the composition of the silicate melt phase. Webster (1997) showed that this apparent "saturation value" increases
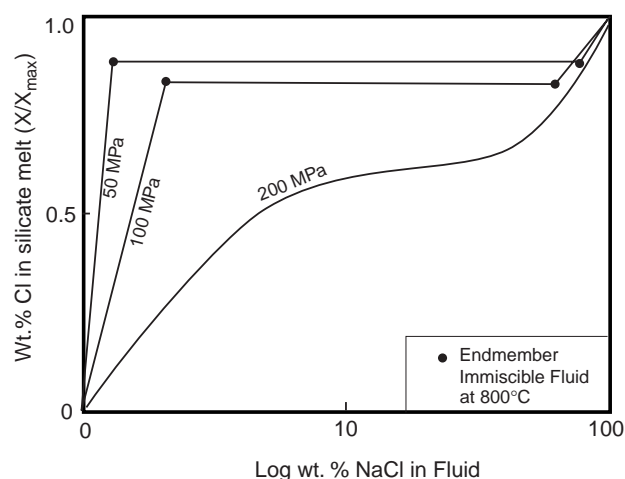

Fig. 3. Relative conc. of Cl in silicate melt versus that in exsolved fluid. Melt conc. is shown relative to the maximum solubility of Cl (X/X_{max}). At 50 and 100 MPa and wt.% Cl in the fluid > 2-3 wt.% (where the NaCl-H_2O system is subcritical) the melt Cl conc. is held fixed by the constant activities and compositions of NaCl in vapor and hydrosaline melt (small black dots). At higher pressures, the solubility curve exhibits non-linearity. Different melt compositions would exhibit similar behavior but with different conc/ of Cl in the melt phase. Schematic plot based on Metrich & Rutherford (1992), Lowenstern (1994), Shinohara (1994) and Webster (1997). End-member NaCl-H_2O fluids from Sourirajan & Kennedy (1962).

with molar [Mg+Na+Fe+Al]/Si in the silicate melt. Therefore, Cl concentrations in andesites and basalts can potentially be higher than the typical ~2700 ppm apparent limit for rhyolites (Metrich & Rutherford, 1992). In reality, though, few magmas have Cl concentrations approaching that of their theoretical maxima because their source regions are low in Cl. Only in rhyolites do concentrations approach those in experimentally Cl "saturated" systems (Metrich & Rutherford, 1992; Lowenstern, 1994; Webster, 1997).

Temperature has little effect on alkali chloride solubility in silicate melts (Webster, 1997) and the effect of pressure is also small. However, pressure has an important effect on the speciation of Cl in the exsolved phase. NaCl has negligible solubility in low pressure vapor and tends to partition into hydrosaline liquid. However, HCl is increasingly favored at low pressures (< 100 MPa; Shinohara & Fujimoto, 1994) and constitutes an important species for Cl transport when magmas degas near

the earth's surface Indeed, HCl is much more abundant than alkali chlorides in volcanic gas.

5. Mixed volatiles: CO_2 vs. Cl

As discussed above, CO_2 exsolves as a gas from magmas and mixes nearly ideally with other gases such as H_2O and SO_2. Cl is less volatile than CO_2, forming species with low vapor pressures. It usually partitions as alkali or Fe chloride complexes, which have limited solubility in exsolving vapors. This can induce unmixing to form separate vapor and hydrosaline melt phases. Coexistence of Cl and CO_2 in the magma further encourages phase separation. For example, in the H_2O-NaCl system at 700°C, fluids with more than 5 wt.% NaCl will unmix to form immiscible vapor and brine phases at any pressure < ~110 MPa (Sourirajan and Kennedy, 1962). However, addition of 20 wt.% or more CO_2 to the fluid will cause unmixing at pressures < ~500 MPa (Joyce and Holloway, 1993). Thus, the conditions where silicic magmas are saturated with both a vapor and brine (hydrosaline melt) will be common in the mid to upper crust. Given the different partitioning behavior of metals between melt, vapor and brine, the presence of CO_2 will increase the likelihood of fractionation of metals among fluids with different densities and transport properties (Candela and Piccoli, 1995).

At present, virtually no experimental data exists for the silicate melt-H_2O-NaCl-CO_2 system. Future studies may provide significant new insights into the role of volatile saturation, phase immiscibility and metal partitioning in the formation of ore-forming hydrothermal fluids.

6. Acknowledgements

7. References

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